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An Overview of Approaches and Current Status

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Abstract

Two principal approaches are identified in the modeling of chemical transformations of SO_x and NO_x in the polluted atmosphere. The fundamental approach involves simulation of the detailed chemical kinetics of the SO_x - NO_x -HC system; in the empirical approach, relatively simple parameterizations of the bulk rates of conversion of precursors to secondary products are sought in terms of environmental factors which, based on laboratory and field measurements, appear to control these rates. In this paper, the principal features of both approaches are described in the form of an overview, with examples of the main results. An assessment is made of the current state of development of both methods, particularly within the context of their applicability in regional transport-transformation models. A brief overview is also presented of the controversial question of linearity of the transformation module with respect to the precursor emissions.

1. INTRODUCTION

Most of the harmful effects of atmospheric sulfur and nitrogen compounds, viz. acidic depositions, visibility degradation, material damage, climatic change, and human health effects, are more directly associated with the secondary products (sulfates and nitrates) of chemical transformations of the precursor emissions (SO_2 , NO, NO_2) into the atmosphere. In the past two or three decades, a great deal of research was focused on these transformation processes, specifically to understand the detailed mechanisms and to obtain quantitative estimates of bulk rates of the conversion of SO_2 to sulfates, and of NO to NO_2 to nitrates, based on laboratory simulations of the polluted atmosphere as well as on field measurements in the real polluted atmosphere. Attempts were also being made to formulate mathematical and numerical models for simulation of the transformation processes. Most recently, a great deal of interest has been aimed at the formulation of the transformation module in meso- and synoptic scale

coupled transport-transformation-deposition models. In this paper, an overview is presented of the current state of development of this module.

Secondary products of chemical transformations of SO_x and NO_x emissions are generally more acidic than their precursors. In the context of acidification of lakes, vegetation and soil, however, the chemical form in which the deposition arrives at the surface is of relatively little significance (because precursor depositions are rapidly converted to the secondary forms following deposition) compared to the fact that the rate of the deposition process itself depends strongly on its chemical form. Thus, for example, sulfate particles are believed to have a considerable longer average atmospheric residence than SO_2 , and hence a larger range of impact. Nitric acid, on the other hand, is likely to be removed from the atmosphere more efficiently and rapidly than its precursors. Consequently, it is necessary for transport-deposition models to distinguish between primary and secondary pollutants, and to facilitate atmospheric chemical transformations through appropriate modules.

The chemical transformation module is an integral part of the overall transport-transformation-removal model. The framework within which the larger model is formulated and solved may be Lagrangian (trajectory), or Eulerian (grid), or some hybrid scheme. Lagrangian or trajectory models simulate the changing concentration field within a given polluted air parcel (e.g., a puff or plume release) as a result of the combined effects of dilution, chemistry, and depositions. Typically, the concentration field as well as meteorological variables are assumed to be homogeneous within the air parcel. Recent attempts have also been made to obtain simulations with finer spatial resolutions within the air parcel. Lagrangian models may be tailored for simulations of pollutant kinetics at the plume scale. Regional Lagrangian simulations are commonly based on simple linear superpositions of individually-calculated concentrations of multiple plumes. Individual plumes may be referred to point sources or area sources. For the modeling of nonlinear processes in multiple interacting plumes over regional scales, Eulerian grid models are more appropriate. They are based on the solution of coupled transport-transformation-removal mass balance equations of individual species over specified two- or three-dimensional spatial grids. Typical grid sizes in regional models vary from 50 to 100 km to a side.

Within each grid cell, pollutant concentrations, as well as meteorological variables, are assumed to be uniformly distributed. In a pure grid model, emissions within a grid cell are considered in an aggregate sense, and are instantaneously homogenized over the entire cell volume. The error of this approximation is particularly severe in two-dimensional grid models which lack vertical resolution. The effects of sub-grid scale processes are sometimes included in terms of bulk parameterizations. Alternately, a hybrid scheme may be used in which individual plumes may be modeled in a Lagrangian sense and detail until they acquire the spatial dimensions of the Eulerian grid size, and subsequent simulation is within the Eulerian framework. The output from a grid model is an evolving series of snapshots of the deposition field over the entire modeled region. This is clearly very desirable in regional modeling. Grid models, however, require far more extensive input information, computations and computational resources than trajectory models, and are generally quite expensive to implement. The chemical transformation module does not depend, per se, on the framework of the larger model formulation. However, its validity does depend on the spatial-temporal resolution of the simulation, and on the facility for accommodating nonlinear processes and plume interactions with its chemically different environment. The remainder of this section is focused on the transformation module.

An objective of this section is to review and assess briefly our present ability to predict the rates of chemical transformations of primary emissions of SO_x and NO_x to secondary acidic products (sulfates and nitrates) during atmospheric transport. Such predictions are based on transformation models, which are mathematical formulations relating secondary pollutant formation rates to concentrations of the precursor gases (e.g., SO_2 , NO), and to any other chemical and meteorological factors considered to contribute to the transformation processes. The principal approaches in formulating such models are discussed for S and N compounds, for power plant and urban plumes, and for each of the major conversion mechanisms believed to be important. Specific formulations of practical interest are reviewed briefly along with their applications, and major outstanding problem areas are identified. An overall assessment is presented of our present standing in terms of the desired goals of transformation modeling. Emphasis is placed on formulations believed to be

suitable for inclusion as transformation modules in current long-range transport-transformation models aimed at simulating regional-scale acidic depositions.

The atmospheric transformation processes are very complex, involving multiple parallel pathways (mechanisms) of physical diffusion and homogeneous and heterogeneous chemical reactions of a wide variety of reactants and catalysts. The reactants may be of primary or background origin or intermediate or secondary products of concurrent reactions. A variety of meteorological factors--UV radiation, temperature, relative humidity, clouds, fogs, atmospheric turbulence, and others -- also have important influence on atmospheric transformation processes. Many of these factors are interdependent; e.g., UV radiation, temperature, clouds, and turbulent mixing are closely related to insolation. Furthermore, a given factor may simultaneously have opposite effects on different chemical reactions; e.g., the effect of plume dispersion should be to "quench" reactions between coemitted species (Schwartz and Newman 1978), but also to promote reactions of primary emissions with background species (Wilson 1978, Gillani and Wilson 1980). Given the complex array of reactants and their reactions influenced in a complicated manner by interdependent environmental factors, one must recognize that no single and simple mathematical expression can describe adequately the transformation processes of a given pollutant. Realistic transformation models should be capable of distinguishing among the different conversion mechanisms and, for each mechanism, should reasonably reflect the dependence of the conversion rate on current plume, background, and environmental conditions.

Historically, the science of transformation modeling is young. As recently as 1977, the state of the art was such that in a widely acclaimed regional monitoring and modeling program, the conversion rate of SO_2 to SO_4^{2-} was represented by a single constant number over a regional scale, regardless of time of day, season, or prevailing meteorological conditions (OECD 1977). Even today, such practice is not uncommon in regional models, perhaps with some justification. Since 1977, however, significant progress has been made in developing transformation modules appropriate for regional models, particularly for the gas-phase mechanism of S conversions. Applicable models for the liquid-phase mechanism are still rare and primitive. Current

transformation models for N compounds are generally complex, requiring extensive computational resources even for mesoscale applications. Their validations are limited.

2. APPROACHES TO TRANSFORMATION MODELING

Basically two approaches to transformation modeling exist--a fundamental approach and an empirical approach.

2.1 The Fundamental Approach

The fundamental approach consists of the so-called "explicit mechanisms method" and its simplified counterparts. In theory, the explicit mechanisms method involves consideration of all significant reactants and their elementary reactions involved in each mechanism of sulfate or nitrate formation. Concentration changes by all chemical reactions are calculated simultaneously for all species at short-term intervals (typically a few seconds). Reactants include not only the precursors (e.g., SO_2 , and NO), their principal oxidizing agents (e.g., OH , HO_2 , and RO_2 in the gas-phase mechanism, and O_2 , O_3 and H_2O_2 in the liquid-phase mechanism), and the secondary products of concern (e.g., H_2SO_4 and HNO_3) but also catalysts and significant intermediate species involved in the mechanisms. Of particular significance are the multitude of reactive HC species and their derivatives involved in gas-phase chain reactions that contribute to photochemical smog formation, as well as to sulfate and nitrate formation. In a spatially homogeneous system (well-mixed plume) consisting of n species, a total of $2n$ first-order, nonlinear, ordinary differential equations must be solved simultaneously at each time step to evaluate the changing species concentrations in the plume and in the background with which the plume interacts. Plume-background interactions must be facilitated in the model. If spatial inhomogeneities are important and need to be resolved, the system of equations becomes substantially larger. Also, because a wide range of reaction-time scales are generally involved, computations for the equations' solutions at each time step are quite involved, time-consuming, and expensive.

Implementation of the explicit mechanisms method has many associated problems. The list of possible reactants is long, and sometimes there is even disagreement about what the products are in given individual reactions. Values of many elementary reaction rate constants have either not been measured or are not quite reliable. Model input requirements also include

specification of initial concentrations of all species in the plume and in the background. While primary emissions from major point sources are reasonably well characterized, area source emissions are not. This is particularly true for the hydrocarbons. Also, the spatial-temporal resolution of the current area source emissions inventories is generally inadequate to verify model performance based on the available mesoscale field data of power plant and urban plume transport and transformations. Atmospheric measurements are either rare or nonexistent for many short-lived species, some of crucial importance (e.g., OH, HO₂, RO₂, and H₂O₂). Detailed HC and aldehyde measurements in the atmosphere are not common. Input specifications and model validations are thus only partial and very approximate.

Perhaps the best example of an attempt to simulate smog chemistry by explicit mechanisms is the work of Demerjian et al. (1974), which incorporated more than 200 species, the great majority of them arising from the explicit use of specific reactive HC and corresponding organic intermediates and sinks. Despite this model's comprehensiveness, the authors warn that its representation of the real atmosphere, which undoubtedly contains hundreds of organic compounds, may be an oversimplification. Such complex chemical modeling is currently impractical for application in regional models. Simplifications and further approximations are necessary. The key is to achieve a reasonable condensation of the vast number of HC and aldehydes, and their reactions, while adequate representation is maintained. Such condensation is attempted either by "lumping" groups of species by some common criterion and then treating each group as a single species in the model, or by substituting a single surrogate species either for all HC (e.g., propylene by Graedel et al. 1976, "nonmethane HC" by Miller et al. 1978) or for a particular lumped group of HC (e.g., xylene for aromatics, by Hov et al. 1977). Two principal methods of "lumping" have been developed: the HSD method (Hecht et al. 1974), and the carbon bond mechanism (CBM) method (Whitten et al. 1980). In the HSD method, organic species of like reactivities are grouped into four main classes: paraffins, aromatics, olefins, and aldehydes. Many models use a modification of this in which the following six lumped classes are used after Falls and Seinfeld (1978) and Falls et al. (1979): ethylene, higher molecular weight olefins,

paraffins, aromatics, formaldehyde, and higher molecular weight aldehydes. In the CBM method, similarly bonded C atoms are lumped into four or more classes. In principle, the CBM is closer to the explicit mechanism and is also easier to use in conjunction with measured data than is the HSD mechanism. Such formulations have been further condensed in specific simulations by reducing the number of species modeled through the use of surrogate reactions and rate coefficients which effectively include the role of the omitted species (Levine and Schwartz 1982).

Validation of simulations performed by detailed chemical models has, to date, been generally based on matching calculated concentrations of certain key aspects of photochemical smog formation (e.g., HC loss, and OH or O_3 formation) with those measured in controlled smog chamber studies in the laboratory. The roles of such meteorological variables as sunlight, temperature, and relative humidity are simulated directly in the experiments and included in the calculations through the dependence of elementary reaction rates on them. The role of other meteorological variables such as turbulence and inhomogeneous mixing generally is not simulated in laboratory experiments. This is probably a serious limitation.

In the real polluted atmosphere, the deficiency of certain key reactive ingredients in a primary emission may well be overcome through entrainment of such ingredients from the background air. The formation of ozone and sulfates in HC-poor power plant emissions in the eastern United States during summer afternoons is thus almost as rapid as in HC-rich urban emissions (Fig. 1, and Gillani and Wilson 1980). Appropriate background characterization and treatment of plume-background interaction can be of critical importance in realistic modeling of transformation processes.

An important positive feature of detailed chemical models is that non-linear chemical couplings between species, including the coupling between sulfur and nitrogen chemistry, is explicitly retained. In this sense, the same model can, in principle, perform simulations of SO_x and NO_x transformations, as well as of urban or power plant plume chemical evolution. With appropriate spatial-temporal resolution, the effect of plume-plume and plume-background interactions can also be performed.

One of the major undesirable features of the detailed chemical approach is the necessity of performing extensive computations. However, considerable differences exist in amounts of computation necessary depending on choice of

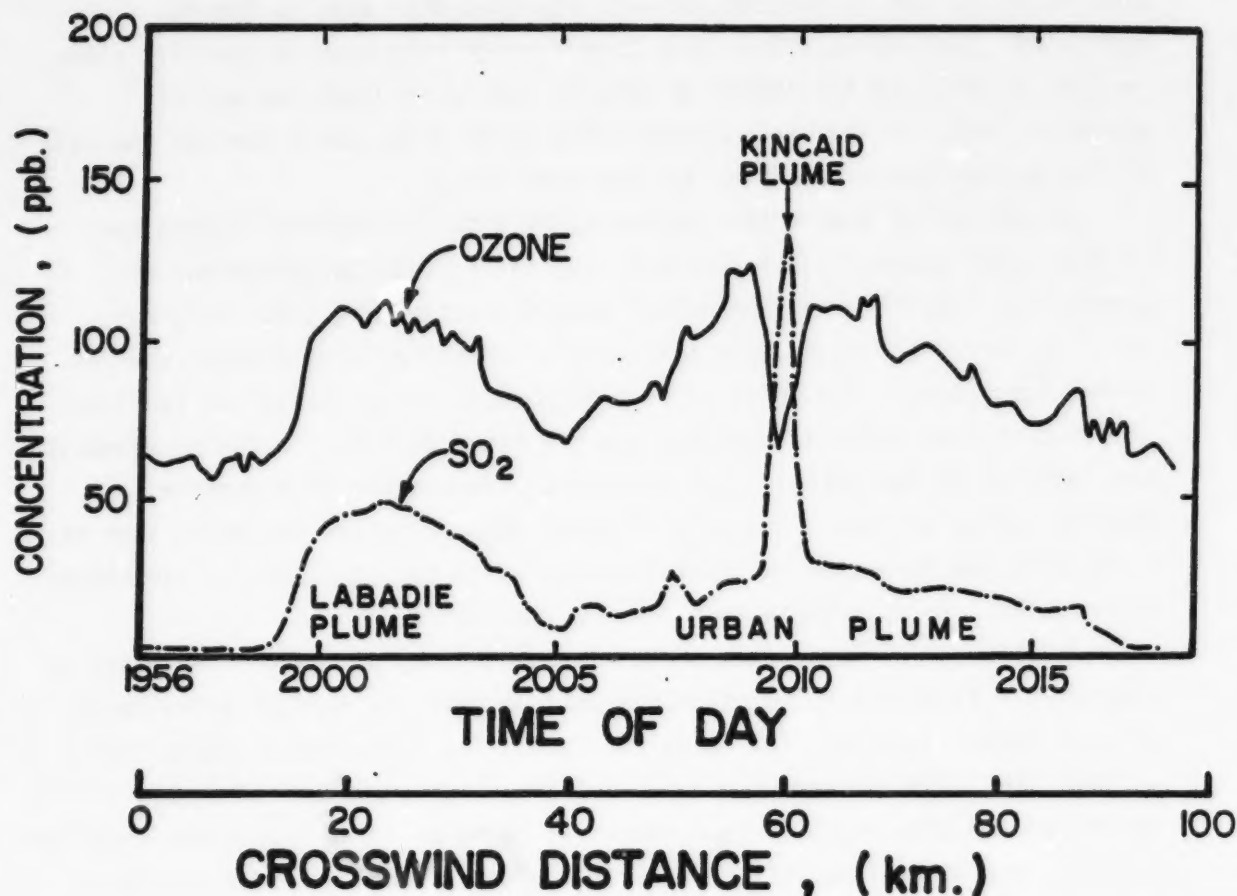


Fig. 1. Crosswind profiles of primary (SO_2) and secondary (O_3) pollutants in the Labadie power plant plume and in the urban plume of St. Louis (including the emissions from a major petroleum refinery complex). The data were collected during an aircraft traverse through the plumes at about 450 m AGL. The plumes were released around midday; the traverse was made around 2000. Observe the comparable levels of excess ozone in both plumes. The Kincaid power plant plume represents a relatively fresh emission into the aged urban plume. Figure is from Gillani et al. (1978).

numerical method and degree of chemical approximations involved. The number of species in the chemical schemes commonly used varies between 10 and 100. The amount of computations increases nonlinearly and rapidly with increasing number of species. For any given chemical scheme of smog simulation, the main numerical problem arises from the fact that the various chemical reactions occur at speeds which vary by several orders of magnitude. This wide range of time scales involved in this problem makes the corresponding set of differential equations quite "stiff." Standard techniques for integrating sets of differential equations (e.g., the Runge-Kutta Method) cannot provide stable solutions of such stiff systems at realistic cost. Special techniques such as those developed by Gear (1971) provide much more efficient numerical integrations by performing automatic time and error control, and are capable of providing accurate numerical solutions, albeit at considerable cost and requiring the use of large high-speed computers. The Gear technique has been used widely in simulations of photochemical smog. Other attempts to reduce computations have resorted to the use of quasi-steady-state assumptions for certain very reactive species. Such assumptions are not always justified and have been shown to lead to large inaccuracies not only under polluted conditions but also in relatively clean background conditions (Farrow and Edelson 1974, Dimitriades et al. 1976, Jeffries and Saeger 1976, Hesstvedt et al. 1978). Judiciously invoked steady-state approximations (QSSA) based on continuous monitoring of pollutant time scales during on-going simulations, can permit locally analytical solutions (Hesstvedt et al. 1978) and even locally linearized analytical solutions (Hov 1983a). Such numerical techniques can provide solutions comparable in accuracy to the Gear solutions at a fraction of the cost, and can be implemented on smaller computers.

Examples of specific detailed chemical model calculations for atmospheric applications are considered in Section 4.1. A recent review paper by (Hov 1983c) is also recommended for those interested in further details pertaining to the fundamental approach to transformation modeling.

2.2 The Empirical Approach

Given the substantial uncertainties and gaps in the input information needed for detailed chemical models, and given the discrepancies in reported transformation rates of SO_x and NO_x , the use of detailed kinetic models continues to be questioned, and simpler empirical rate expressions are often

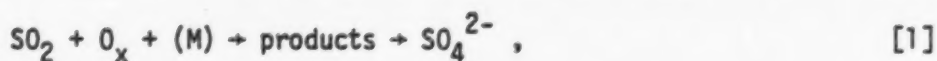
avored. A great deal of experimental research on chemical transformations has been directed at obtaining estimates of the conversion rates of SO_2 to sulfates, and of NO_2 to nitrates in the laboratory and in the field. In recent years, some success has been achieved in relating field estimates of the conversion rates to specific conversion mechanisms and to specific, measured influencing factors. A large number of source-related and environmental factors have been implicated as influencing transformations. They include the time and height of source release, the nature and amounts of the acid precursors, other coemitted species, the reactivity of the air mass in which emissions are transported, as well as such meteorological factors as sunlight, temperature, absolute humidity, clouds and fogs, and atmospheric stability.

In the empirical approach, an attempt is made to identify the rate-controlling factors for each mechanism and to formulate and validate an overall rate expression for measured sulfate or nitrate formation by each mechanism directly in terms of these factors, which are also measured. In other words, the effect of the multiple elementary reactions is parameterized in terms of pertinent, measurable chemical and meteorological factors. Such parameterizations of the conversion rate are simple rate expressions, which can be inserted directly into regional models as the transformation module. They entail very few computations and require inputs that are, for the most part, relatively readily available even on a regional scale. In spite of their simplicity, they often yield quite reliable estimates of actual atmospheric formations of such final products as sulfates. This is particularly true when their formulation is based directly on field data and their application is based on measured input data. Their principal disadvantage is that they lack generality, being applicable mainly under environmental conditions reasonably close to those for which they have been successfully validated. In specific applications for which relevant parameterizations are available, their simplicity and reliability make them immensely valuable.

The existing empirical parameterizations of sulfur chemistry are largely based on mesoscale plume data. At least three important practical implications of this limitation may be identified. First of all, given the dominance of source-specific characteristics in mesoscale plume transport, empirical parameterizations which are mesoscale in origin must be considered to be

specific to the source type (e.g., power plant plumes versus urban-industrial plumes) for which they were developed. Secondly, since the characteristic time scales of the atmospheric residence of secondary pollutants such as sulfates and ozone are significantly longer than mesoscale, it must be presumed that the parameterizations for plumes would be sensitive to boundary conditions. In fact, empirical observations have shown that sulfate and ozone formation rates in power plant as well as urban plumes are strongly sensitive to the chemical condition of the background air, and to the rate of plume dilution by entrainment of this background air (Gillani and Wilson 1980; Miller and Alkezweeny 1980). Plume-background interactions can sometimes even obscure the initial chemical distinctions between a power plant plume and a petroleum refinery plume (see Fig. 1). Finally, one must question the validity of empirical parameterizations of mesoscale origin in synoptic scale applications. On the positive side, however, it has been demonstrated empirically that pollutant plumes evolve to the chemical maturity characteristic of regional air masses within only a few hours of transport during sunny convective conditions typical of summer days in the eastern United States (Gillani and Wilson 1980). At least under such conditions, chemical parameterizations derived from data of chemically aged plumes may have validity even during long range transport.

The reactions governing SO_2 oxidation have the general form:



where O_x represents the principal oxidizing agents; i.e., OH and possibly HO_2 and RO_2 for gas-phase oxidation (Calvert et al. 1978), and H_2O_2 , O_3 , and O_2 for liquid-phase oxidation (Penkett et al. 1979); (M) represents the catalysts, if and when any are involved. With the possible exception of catalyzed reactions (Freiberg 1974), the rate of sulfate formation, r_s , may be expressed as:

$$r_s = \frac{\partial}{\partial t} (\text{SO}_4^{2-}) = k_s \cdot (\text{SO}_2) \quad [2]$$

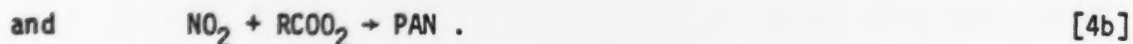
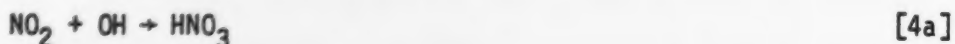
where the fractional conversion rate, k_s , depends on O_x , the oxidizing species. Such a relationship is valid as long as SO_2 is not in stoichiometric excess. The validity and linearity of this equation are further discussed in Section 3. Parameterization of k_s which is the goal of

empirical transformation models, is thus a representation of the weighted contributions of factors which effectively determine the O_x concentrations. It may be broken down by mechanisms into:

$$k_s = k_{sG} + k_{sL} + k_{sHET} \quad , \quad [3]$$

where components on the right hand side represent, respectively, the fractional conversion rates by gas-phase, liquid-phase, and heterogeneous aerosol surface reaction mechanisms. No parameterizations have been attempted for the heterogeneous mechanism, partly because reliable and particular atmospheric data are lacking and partly because the mechanism generally is not considered important on the regional scale. Specific parameterizations of S conversions are most developed for k_{sG} , and efforts to parameterize k_{sL} have just begun. These are discussed in the next section.

Similarly, the formation of the two principle secondary nitrates (HNO_3 and PAN) are largely governed by the reactions



Hence, their formation rates may be expressed as:

$$r_{HNO_3} = k_{HNO_3} \cdot (NO_2) \quad [5a]$$

$$r_{PAN} = k_{PAN} \cdot (NO_2) \quad , \quad [5b]$$

where the fractional conversion rates, k_N ($N = HNO_3, PAN$), depend on the concentrations of OH and $RCOO_2$, respectively. The parameterizations of k_N would represent the weighted contributions of the factors which effectively determine these free radical concentrations. Empirical parameterizations of k_N based on field data have not been formulated or tested. Sensitivity of k_N to the HC - NO_x mix has been studied in smog chamber experiments. Some of the most recent specific results and their implications will be discussed in a later section.

3. THE QUESTION OF LINEARITY

A much debated matter, and one of considerable practical importance in terms of regional modeling and control strategy, is the question of linearity (or the lack of it) in the source-receptor relationships between emissions of SO_x and NO_x and their depositions. An important subset of this larger question pertains to the linearity of relationships between r_s and SO_2 , and r_N and NO_x . In this section, the discussion is limited to the question of linearity of the chemical transformation processes. If the transformation chemistry is nonlinear, certain common modeling practices based on the assumption of linearity must be viewed with caution. For example, regional models typically have a spatial resolution over grids of 50 to 100 km to a side. The assumption of uniform species concentrations within a grid cell which includes concentrated emissions sources may give erroneous transformation estimates unless some appropriate parameterization of sub-grid scale processes is included. Distinctions in the chemical mix of different source emissions are also presumably important in the case of nonlinear chemistry. Linear superpositions of species concentrations, calculated for individual plumes assumed to be isolated, will also give erroneous estimates of nonlinear secondary formations in regions with multiple plume interactions. The validity of the linearity assumption is also crucial to the success of attempts to control secondary pollutants by a strategy of linear rollback of precursor emissions.

The lack of consensus on the question of linearity, particularly with respect to sulfur chemistry, is probably due to different interpretations of the definition of the term linear relationship. By definition, the relationship between r_s and SO_2 is linear if it can be stated in the form of Equation [2], and if k_s is independent of SO_2 . Clearly, k_s is variable through its dependence on species such as the OH free radical which are responsible ultimately for the oxidation of SO_2 . Therefore, the critical question is whether these oxidizing agents are themselves dependent on SO_2 . There is no doubt that in a fresh plume with high concentration of SO_2 , OH level is significantly controlled by SO_2 itself, and the oxidation of SO_2 is a nonlinear process. Such conditions, however, are short-lived. Subsequently, if there are no further fresh injections of SO_2 into this plume, the formation of OH will be governed by the NO_x -HC chemistry in the plume

and by entrainment from the background of OH itself and of other reactive species contributing to OH formation. The direct dependence of plume NO_x -HC chemistry on local SO_2 concentration is very weak in this stage of plume transport. Consequently, one commonly finds in the published literature explicit or implicit statements about linear sulfur chemistry under such conditions. If the mathematical definition of linearity is to be interpreted strictly, such statements are correct within the context of the transport of a particular plume release. In the broader context of modeling of longer-term averages or continuous emissions, possibly varying with time, and with inevitable plume-plume and plume-background interactions, an indirect form of nonlinearity does exist because of the correlation between SO_2 emissions and the co-emissions of NO_x and HC. A broader definition of linearity which requires k_s to be independent not only of SO_2 but also of co-emitted species is implicit in the works of Cahir et al. 1982 and Hidy 1982.

The significance of the role of the co-emitted species is illustrated in the following practical example. Suppose we wish to answer the following question: "Will a 50 percent reduction of SO_2 emission from source A (or region A) result in a corresponding 50 percent decrease in downwind sulfate formation?" There is no unique answer to this question. First, the manner in which the emission reduction is achieved is important. If source A is a coal-fired power plant, and the reduction in SO_2 emission is achieved by a 50% reduction in the amount of fuel burned, there may also be an accompanying reduction in NO_x emissions which, in turn, will cause k_s to be different. The answer to the question, therefore, is "no". The cause of this apparent or effective nonlinearity is the indirect dependence of k_s on SO_2 through the correlation between co-emitted SO_2 and NO_x . The 50 percent reduction in SO_2 emission could also have been achieved by the use of fuel of 50 percent lower sulfur content or by scrubbing SO_2 from the combustion products prior to stack emission. To the extent that these latter procedures may not have changed NO_x emissions, k_s will remain unchanged except during initial transport, and the downwind sulfate formation would be expected to decrease by about 50 percent, all other conditions being the same. The answer to the question is therefore "yes."

A second factor which will profoundly influence downwind sulfate formation is the composition of the air which the plume encounters during mesoscale and long range transport. There is field evidence to suggest that the role of

co-emitted species may be substantially enhanced, or overwhelmed, by the role of the background air which the plume entrains by mixing processes. Like the co-emitted species, a polluted background can also serve as the source of the oxidizing agents. Figure 1 shows an example of the side-by-side transport of two St. Louis plumes of very different emission composition, yet comparable secondary formations. The Labadie power plant emission is characterized by a very low HC/NO_x ratio. The urban plume of St. Louis, including the emissions from a large petroleum refinery complex, by contrast is much richer in reactive HC emissions. The secondary formation of ozone in large plumes on summer days is closely related to the formation of sulfates (White et al. 1976, Gillani and Wilson 1980). The formation of ozone and sulfates in power plant plumes at rates comparable to those in urban plumes is due to the entrainment of polluted background air. During long-range transport, the role of the background air may well predominate as a source of reactive species which oxidize SO_2 . In laboratory measurements with no role of a variable background, a first order dependence of sulfate formation on SO_2 concentrations has been observed for gas-phase reactions (Miller 1978) as well as liquid-phase reactions (Penkett et al. 1979). Mesoscale field measurements are also generally consistent with pseudo-first-order dependence between r_s and SO_2 , except during early transport.

A common practice in detailed models of sulfur chemistry in the atmosphere is to represent the $\text{SO}_2 + \text{OH}$ reaction as a terminal reaction, effectively leading to the formation of H_2SO_4 and depletion of the OH radical concentration. This dependence of OH on SO_2 therefore contributes to nonlinearity of the sulfur transformation process. It has been pointed out recently (Stockwell and Calvert 1983) that the SO_2 -OH reaction may initiate a chain of reactions which may lead not only to formation of H_2SO_4 , but also to regeneration of OH in the presence of NO_x and hydrocarbons. Such recycling of OH would have the effect of weakening the nonlinearity of sulfur chemistry. An important conclusion of the recent NAS report on acid deposition (NAS 1983) was indeed that nonlinearity of sulfur chemistry is probably quite weak, and that even the broader coupling between sulfur emissions and depositions may be substantially linear on a long-term average basis over the spatial scale of eastern North America.

Based on theoretical considerations, the relationship between r_N and NO_x is expected to be nonlinear, since k_N depends on OH, for example, which depends directly on the NO_x chemistry. Results of recent smog chamber experiments suggest, however, that the nonlinearity of r_N may also be short-lived relative to the time scale of long-range transport (Spicer 1983). Pseudo-first-order parameterizations of r_N may be justifiable, but k_N may also need to reflect the make-up of the air which an emission encounters during transport.

4. SOME SPECIFIC MODELS AND THEIR APPLICATIONS

4.1 Detailed Chemical Simulations

Detailed chemical modules based on the explicit mechanisms approach have been used within Eulerian as well as Lagrangian formulations, and in model applications at the plume scale as well as the regional scale. Such transformation modules differ principally in terms of their representations of the hydrocarbons, and in the methods used for the numerical solution of the set of nonlinear differential equations describing the species concentration changes by chemical reactions. The following discussion outlines some specific representative models, and is not intended as an extensive review of chemical models.

The LIRAQ model (McCracken et al. 1978, Duewer et al. 1978) is an example of a two-dimensional grid model (single well-mixed vertical layer). The transformation module attempts to simulate photochemical smog formation based on the HSD scheme (Hecht et al. 1974), and the numerical solution is based on the Gear technique. The SAI Airshed Model (Reynolds et al. 1979) is a three-dimensional grid model which permits initial isolation of elevated point sources from surface sources. It uses the carbon bond mechanism of photochemical smog simulation (Whitten and Hogo 1977), and numerical solution is by a finite difference technique (SHASTA) developed by Boris and Book (1973). An ambitious three-dimensional regional grid model currently under development at EPA (Lamb 1981) presently uses the chemical scheme of Demerjian and Schere (1979) which uses four hydrocarbon classes of different reactivities. In some regional models (e.g., McRae et al. 1979), point source plumes are simulated in a Lagrangian sense within the framework of an Eulerian grid network until they attain the dimensions of the grid cell. Thereafter, the simulation is continued in the Eulerian frame.

On a global basis, the troposphere is presumed to be clean and the organic species most relevant to smog formation are carbon monoxide (CO) and methane (CH₄). Recently, a two-dimensional global model was employed by Fishman and Drutzen (1978) to predict the global distribution of OH, HO₂, and CH₃O₂ radical concentrations. Predicted OH concentrations were reasonably comparable with recent, measured atmospheric concentrations (Sheppard et al. 1978). Altshuller (1979) used this model for OH to investigate the variability of the sulfate formation rate by the homogeneous gas-phase mechanism with respect to latitude and altitude. His results showed that in the clean environment, OH is the principal oxidizing agent, and that, at higher latitudes, e.g., in the northeastern United States, Canada, and northern Europe, large seasonal differences in sulfate formation by this mechanism are to be expected. Very little sulfate formation is likely in winter by gas-phase mechanisms.

The regional model of Carmichael and Peters (1979) is based on the chemistry of a clean background in which the only organic species are CO and CO₂. They invoke the pseudo-steady-state assumption for the oxidizing species OH, HO₂, H₂O₂, and O₃, and use their iterative solution for these species in first order expressions for the oxidation of SO₂ to estimate the sulfate formation rate.

Most plume simulations are based on trajectory-type models. Calculations made for polluted industrial regions and urban areas have simulated certain observed phenomena related particularly to O₃ behavior (Graedel et al. 1978) but at the same time have yielded conflicting results concerning important control strategies. Results by Graedel et al. (1978) suggest OH levels to be directly proportional to NO₂ levels, implying that reduction of NO_x emissions would help control nitrate and sulfate production. Miller (1978) showed rather that NO_x emissions tend to delay SO₂ oxidation and that the ratio (NMHC/NO_x) of initial concentrations of nonmethane HC's and NO_x's dominates the SO₂ oxidation rate. Miller's conclusions were verified experimentally. Actually, as suggested by Miller (1978), precursor effects may significantly differ in the first several hours of daytime plume transport from their effects during subsequent regional transport.

Detailed chemical calculations also have been applied to simulate sulfate and nitrate formation in urban plumes (Isaksen et al. 1978, Miller and Alkezweeny 1980, Bazzell and Peters 1981) and in power plant plumes (Miller

et al. 1978, Bottenheim and Strausz 1979, Levine 1980, Hov and Isaksen 1981, Stewart and Liu 1981). In these calculations, proper simulations of the changing background air and of plume-background interactions were necessary for at least qualitative agreement with field observations. Levine (1980) neglected plume-background interactions and, as a result, his conclusion that power plant plume dilution inhibits sulfate formation is contrary to field observations in moderately polluted regions (Gillani and Wilson 1980). Hov and Isaksen (1981), on the other hand, treated crosswind spatial inhomogeneities in sulfate formation resulting from plume-background interaction and succeeded in simulating, at least qualitatively, many features of the crosswind plume data of Gillani and Wilson. Stewart and Liu (1981) similarly provided cross-wind resolution and plume-background interactions with their reactive plume model which was based on the carbon-bond mechanism for the simulation of chemical kinetics. Recently, Hov (1983b) performed a plume simulation in which vertical stratification of the concentration field was considered. In general, plume simulations have indicated that O_3 and aerosol formation are greater when the background is polluted, that OH is the dominant oxidizing species for SO_2 and NO_2 , and that OH and peroxy radical (HO_2 , RO_2) concentrations, which play an important role in O_3 formation, peak at midafternoon in polluted regions.

In all of the above simulations, only the homogeneous gas-phase chemistry was included. Rodhe et al. (1979) added reactions of SO_2 and NO_2 with H_2O_2 in the presence of "clouds" to a highly lumped gas-phase chemistry model. H_2O_2 generation was calculated based on the gas-phase reactions. The authors recognized qualitatively that the effective rate constants for cloud reactions must include not only the effect of the liquid-phase transformations occurring in cloud droplets and in precipitating clouds, but also exchange rates of the reacting species between the droplets and the surrounding air, and the frequency and occurrence of clouds and precipitation. They then proceeded to choose rate constant values such that overall gas- and liquid-phase oxidation rates of SO_2 became comparable and the liquid-phase oxidation of NO_2 became relatively insignificant compared to its gas-phase counterpart. This procedure for the liquid-phase mechanism represents a highly parameterized approach, with parameter values assumed rather subjectively. Their calculations were applied regionally to the European industrial environment under

summertime conditions. The relative contributions of gas-phase and liquid-phase mechanisms to sulfate and nitrate formation, of course, reflected their assumptions.

4.2 Parameterized Models

For many years, no consensus could be reached concerning the relative importance of the many chemical and meteorological factors implicated as influencing gas-to-particle S conversion. Most transport-transformation models used constant pseudo-first-order rates for the oxidation of SO_2 . Documentation of sunlight as a dominant environmental factor governing sulfate formation in power plant plumes (Gillani et al. 1978) has since been verified and widely accepted and used. In particular, in a recent review of field data on sulfate formation in power plant plumes during all seasons in the United States, Canada, and Australia, Wilson (1981) observed that the outstanding common pattern in this broad data base was the diurnality of the sulfate formation directly related to solar radiation. Such a role of sunlight is also consistent with the observed distinct summer peak in regional SO_4^{2-} distribution in the eastern United States (Husar and Patterson 1980), even though corresponding SO_2 emissions are distributed fairly uniformly over all seasons (DOE 1979).

A sunlight-dependent model of the form $k_s \propto R_T$, the total incoming solar radiation flux at ground level, was used by Gillani (1978) in a diagnostic mesoscale plume model and by Husar et al. (1978) in a multiday plume S budget study. A similar parameterization has been used by Shannon (1981) and by others. Gillani found that such a model based only on sunlight could not simulate the observed day-to-day variation in sulfate formation. Evidently, factors other than sunlight must be included. Also, the manner in which sunlight influences the conversion process must be more carefully considered. As Wilson (1981) noted, observed correlations of the conversion rate with sunlight, or with air temperature (Eatough et al. 1981), do not imply the direct role of these factors in the underlying mechanisms. These two factors are highly correlated, as are both to turbulent mixing, convective cloud formation, and a number of other factors, which alone can exert rate-controlling influences on specific conversion mechanisms. Accordingly, formulation of meaningful parameterizations must be based on mechanistic considerations.

Gillani et al. (1981) recently advanced a parameterization of the gas-to-particle S conversion by the gas-phase mechanism based on plume data collected during the summer in the Midwest (Missouri and Tennessee). The motivation for their gas-phase parameterization was derived from their earlier identification of a recurrent pattern of O_3 and aerosol generation in power plant plumes, which evidently involved participation of reactive species entrained from the background (Gillani and Wilson 1980). Gillani et al. argued that accelerated photochemical generation of the radical species OH, HO_2 and RO_2 that oxidize gas-phase SO_2 would be facilitated by reactions involving NO_x emissions and entrained reactive HC and free radical species. Consequently, the quality of the background air and the extent of plume dilution by its entrainment were judged to be important contributing factors, in addition to sunlight which powers the photochemical reactions. Given the lack of detailed data of the oxidizing species, the authors resorted to using O_3 as a surrogate for, or an indicator of, air mass reactivity. Vertical plume spread, Δz_p , was chosen as a measure of the extent of plume dilution. The resulting gas-phase parameterization is:

$$k_{sG} \approx (.03 \pm .01) R_T \cdot (\Delta z)_p \cdot (O_3)_0, \quad [6]$$

where k_{sG} is in percent hr^{-1} , R_T is in $kW m^{-2}$, $(\Delta z)_p$ is in meters, and

background ozone, $(O_3)_0$, is in ppm. The coefficient 0.03 ± 0.01 was chosen on the basis of the best fit between the calculated (Equation 6) and measured values of k_{sG} . The measured values were for dry (relative humidity < 75

percent), cloudless conditions when gas-phase reactions may safely be assumed to predominate. The parameterization was validated successfully by data collected in the plumes of three large central power generating stations in Missouri and Tennessee during two different summers. The empirical coefficient (0.03) thus pertains to such large power plant plumes in which the initial NO_x/SO_2 ratio is about 1:3.

The above parameterization is believed to provide good estimates of the gas-phase sulfate formation rate under the moderately polluted conditions characteristic of the eastern United States in summer and appears to be valid even under more polluted conditons during stagnation episodes. Its validity

in winter, even in this region, remains to be tested. Its performance in clean regions such as the Southwest, and in extremely polluted areas such as Los Angeles, CA, on a smoggy day is also unproven. Furthermore, the parameterization has no validity for urban plumes and possibly also plumes from small power plants owing to substantially different composition of the emissions. In spite of these restrictions, the parameterization is of practical significance. Its input requirements are minimal and can be satisfied presently over a regional scale in the eastern United States. Its explicit inclusion of plume-background interactions and air mass conditions probably gives it some validity even during long-range transport when the role of the background is expected to be dominant. Application of the parameterization based on 1976 St. Louis, MO, data of the input variables yields the diurnal and seasonal pattern of k_{SG} as shown in Figure 2. The magnitudes and temporal variations

shown are plausible and consistent with available field data, as well as with expectations based on detailed chemical calculations (Calvert et al. 1978, Altshuller 1979). The results predict that in the Midwest, gas-phase mechanisms may be expected to convert about 10 to 20 percent of the SO_2 in a power plant plume to SO_4^{2-} during an average summer day, while corresponding conversion in winter may be about an order of magnitude smaller. By comparison, measured values of SO_2 to SO_4^{2-} conversion by all mechanisms range between 15 and 35 percent for summer conditions in the same region (Gillani and Wilson 1983). It may be inferred, therefore, that liquid-phase mechanisms may convert about 5 to 15 percent of the SO_2 to SO_4^{2-} per day during summer in the Midwest.

Gillani et al. (1983) have recently also made a first attempt to formulate a parameterization of liquid-phase SO_4^{2-} formation resulting from plume-cloud interactions. The formulation explicitly recognizes that the overall conversion rate, k_{SL} , depends not only on the chemical reaction rate within cloud droplets, K_{SL} , but also on the physical extent of plume-cloud interactions.

Because clouds are discrete entities in space and time, and plume-cloud interactions are somewhat random events, the authors choose to describe plume-cloud interactions in probabilistic terms. The overall formulation has the general form

$$k_{SL} = P \cdot K_{SL} \quad [7]$$

AVERAGE CONVERSION DAY OF MONTH 1976 St Louis Data

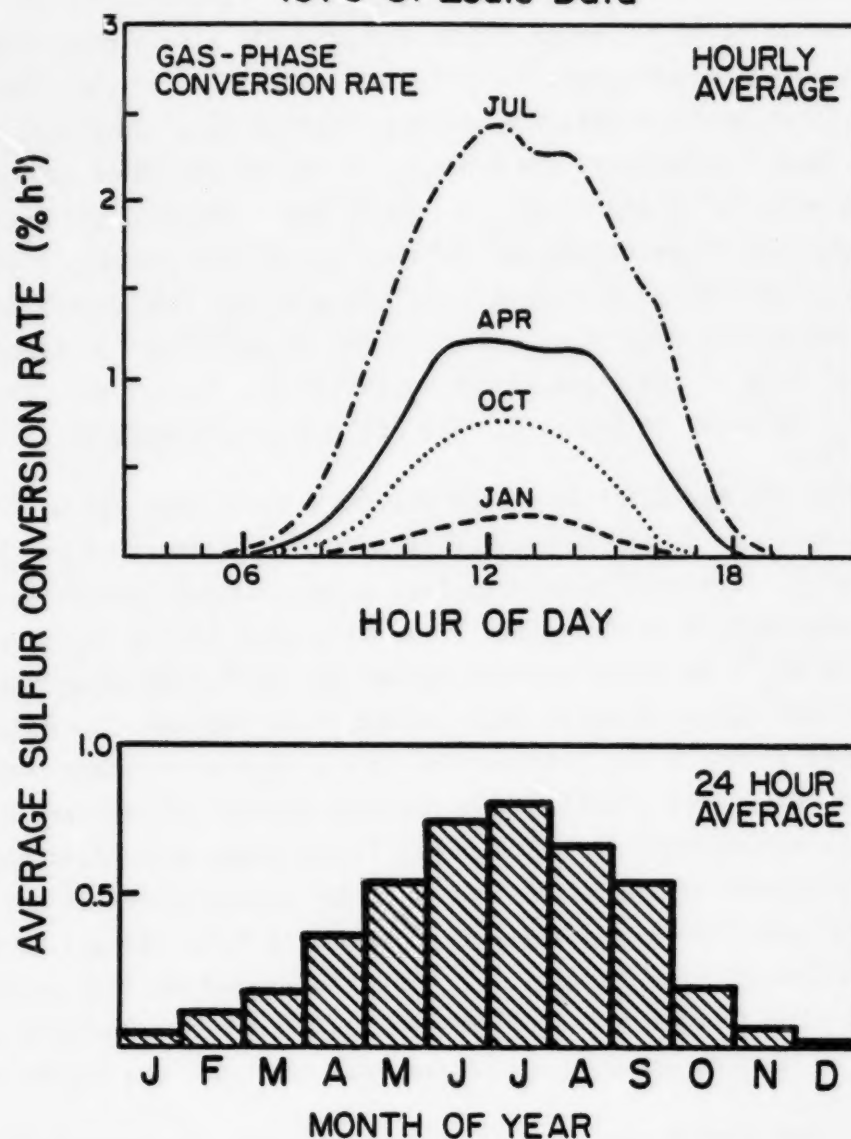


Fig. 2. Diurnal and seasonal patterns of the gas-to-particle conversion of sulfur by gas-phase mechanisms, according to calculations based on the parameterization of Gillani et al. (1981).

where P represents a measure of the probability and extent of plume-cloud interactions. All three quantities in the equation are time dependent. The dependence of P on local plume and cloud dimensions has been derived explicitly (details given in original reference), and its values are determined during an actual power plant plume model run based on current, calculated plume dimensions and local cloud data from surface weather observations of the National Weather Service network of stations, as well as on local lidar and aircraft measurements. P represents a measure of the fraction of a given plume volume which is in contact with the liquid phase.

The authors did not attempt to parameterize K_{SL} . It depends on such variables as liquid water concentration, droplet pH, and concentrations of dissolved S, oxidizing agents (H_2O_2 , O_3 , and O_2), and catalysts (Fe and Mn). No data were available for such cloud chemical composition. The authors did, however, obtain an average daytime estimate for K_{SL} under typical summertime fair-weather convective cloud conditions in the Kentucky-Tennessee area. The inferred value of K_{SL} (summer daytime average conversion rate within clouds was 12 ± 6 percent hr^{-1}). This value compares with values of 0 to 104 percent hr^{-1} estimated by Hegg et al. (1980), based on ambient SO_2 and SO_4^{2-} measurements in wave cloud situations and with predicted values ranging from 10 to 20 percent hr^{-1} in large storm cloud systems in the summer based on an indirect mass balance technique (Scott 1981). Also, the value of P averaged over 24 hr is expected to be significantly less than 0.1 during summer as well as winter. In other words, the average bulk plume conversion rate by liquid-phase mechanisms is likely to be less than the local droplet-phase conversion rate by more than an order of magnitude. All of these estimates involve several assumptions and approximations and must be used with caution. Values of K_{SL} at night and in winter are believed to be substantially smaller as a result of lower concentrations of the photochemically generated oxidizing species, O_3 and H_2O_2 .

Based on the above parameterizations and St. Louis, MO data, it is estimated that the 24-hr average, overall sulfate formation rates in July are likely to be 0.8 ± 0.3 percent hr^{-1} by gas-phase reactions and at least

0.4 ± 0.2 percent hr^{-1} by liquid-phase reactions. Winter rates by gas-phase reactions are estimated to be an order of magnitude smaller than in summer and by liquid-phase reactions are estimated to be comparable during the two seasons.

A variety of empirical data suggests that liquid-phase conversions in wetted aerosols may be significant at relative humidity between 75 and 100 percent (Dittenhoefer and de Pena 1980, McMurry et al. 1981). Winchester (1983) has formulated the following empirical parameterization of k_s which highlights the role of absolute humidity and temperature:

$$k_s \propto (P_{\text{H}_2\text{O}})^{3.08} (P_{\text{H}_2\text{O},\text{sat}})^{1.213}, \quad [8]$$

where $P_{\text{H}_2\text{O}}$ denotes the partial pressure of water vapor, and $P_{\text{H}_2\text{O},\text{sat}}$ denotes the saturation vapor pressure of water vapor (a measure of temperature).

No comparable parameterizations of NO_x transformations have been formulated. Summertime plume measurements suggest that NO_3 formation is primarily in the form of HNO_3 vapor (Forrest et al. 1979, 1981; Hegg and Hobbs 1979; Richards et al. 1981) and that oxidation of NO_2 to HNO_3 may proceed about three times faster than does oxidation of SO_2 to H_2SO_4 (Forrest et al. 1981, Richards et al. 1981). Gas-phase mechanisms of HNO_3 formation are believed to predominate in the summer.

Whitby recently used a simple model assuming the total accumulation mode aerosol formation rate to be directly proportional to UV radiation intensity, to simulate observations of aerosol formation in the St. Louis, MO, urban plume of 18 July 1975. He estimated that about 1000 tons of secondary fine aerosol may be produced in the St. Louis plume in one summer irradiation day (Whitby 1980). For the same plume transport, Isaksen et al. (1978) used a detailed chemical model to simulate the measured data of O_3 and SO_4^{2-} formation presented by White et al. (1976) and estimated peak H_2SO_4 and HNO_3 formation rates of 5 and 20 percent hr^{-1} , respectively, to occur in the early afternoon. Alkezweeny and Powell (1977) also measured the St. Louis plume and estimated afternoon SO_4^{2-} formation rates to be 10 to 14 percent hr^{-1} . Miller and Alkezweeny (1980) measured SO_4^{2-} formation rates in the Milwaukee urban plume, particularly related to the quality of the background air mass, to range from 1 to 11 percent hr^{-1} .

Spicer (1977) estimated the NO_2 -to-products transformation rate in the Los Angeles urban plume as $10 \pm 5\% \text{ hr}^{-1}$. In more recent measurements downwind of Los Angeles (Spicer et al. 1979), the observed lower limit of NO_x conversion rates ranged from 1 to 16% hr^{-1} , with typical rates in the 5 to 10 percent hr^{-1} range. Spicer (1980) estimated NO_x transformation/removal rate for the Phoenix urban plume to be less than 5 percent hr^{-1} , while data for Boston showed rates in the 14 to 24 percent hr^{-1} range. Transformation products of NO_x transformations include not only inorganic nitrate (e.g., HNO_3), but also organic species (e.g., PAN). Spicer attributes the low conversion rate in Phoenix at least partly to thermal decomposition of PAN and its analogs at the high ambient temperatures of the desert area.

Recently, Middleton et al. (1980) performed a model study of relative amounts of sulfate production in wetted aerosols in a polluted environment by two different mechanisms: condensation of SO_2 gas-phase oxidation products, and catalytic and noncatalytic SO_2 oxidation in the liquid phase. The microphysical vapor transfer to the aerosols and the chemical conversion within the aerosols were treated as coupled kinetic processes. Concentrations of the oxidizing species (e.g., OH, and H_2O_2) and of the catalysts (e.g., Fe, Mn, and soot) were assumed known, and representative values for day and night and summer and winter were used. The study concluded that in the daytime, photochemical reactions and liquid-phase oxidation by H_2O_2 are likely to predominate, with particle acidity playing a minor role. At night, sulfate production rates are low, being principally by catalytic and noncatalytic liquid-phase mechanisms involving O_3 and O_2 . The daytime H_2O_2 reaction rate was enhanced by the lower winter temperatures.

5. SUMMARY AND CONCLUSIONS

Transformation models can, at best, be only as good as our understanding of the transformation processes. Significant gaps in this understanding remain, particularly with respect to physical and chemical kinetics of the liquid-phase processes. The validity and extrapolation of laboratory results to real atmospheric conditions are often questionable. Field measurements, in general, are insufficient, particularly for wet conditions. For example, simultaneous physical and chemical measurements pertaining to plume-cloud interactions are almost nonexistent.

Detailed chemical models are not yet practical for application in regional models to predict acidic product formation and deposition. Many individual pieces of information--microphysical pathways and chemical reactions--must be put together correctly and we are still struggling to assemble an adequate information base about the individual pieces. To complicate matters, important couplings exist between the different major mechanisms of sulfate and nitrate formation (e.g., H_2O_2 formed by gas-phase photochemistry is of paramount importance in liquid phase chemistry), and significant interdependences exist among the major influencing environmental factors.

Considerable progress has been made in transformation modeling in recent years. Significant gaps remain, however, in our ability to predict transformation rates of SO_x and NO_x under atmospheric conditions. The following observations summarize the current status of the principal aspects of transformation modeling:

- It is now possible to simulate the principal features of the smog chamber chemistry of the SO_x - NO_x -HC system rather accurately by detailed modeling of the chemical kinetics based on lumped representations of the hydrocarbons, even though details of the chemical mechanisms are not fully understood.
- Detailed chemical models of plume transformations under atmospheric conditions have successfully simulated many qualitative features of field observations, including some details of crosswind profiles influenced by plume-background interactions. These simulations are mainly restricted to gas-phase chemistry.
- The principal current limitations in detailed chemical modeling are probably related to inadequate characterization of the emission field and of the ambient polluted regional background. Improved and more detailed inventories of the emissions of SO_x , NO_x , and HC from major sources including the urban area sources, and reliable measurements of reactive species (e.g., OH, RO_2 , H_2O_2) in the ambient atmosphere are needed before reliable conclusions concerning the regional-scale transformation processes can be made. The relative importance of co-emissions vs background entrainment as sources of oxidizing agents (OH, RO_2 , H_2O_2 , etc.) is not fully understood at the present time.

- Current detailed chemical models generally do not include liquid-phase chemistry. Quantitative descriptions of the liquid-phase environment (e.g., cloud dynamics, plume-cloud interaction, etc.) are not adequately incorporated into transformation models. Cloud and fog chemistry measurements are sparse and much needed. Coupled modeling of gas- and liquid-phase chemistry is necessary, particularly under summer conditions. First steps in this direction have been taken.
- For the near future, it appears that transformation modules based on empirical parameterizations will continue to predominate in operational regional models. All models, to varying degrees use parameterizations based on laboratory and field data. Currently, regional models mostly employ pseudo-first-order or constant first order bulk conversion rates. Preliminary parameterizations have been developed only for sulfate formation in power plant plumes, and will undoubtedly continue to be improved. No practical parameterizations exist yet for nitrate formation or for urban plumes.
- The basis for refining these estimates to reflect at least the gross diurnal and seasonal variations, and even the role of a changing background, exists. Increasingly, new models are incorporating such empirical expressions, which are constantly being improved. The state-of-the-art of such parameterizations will be further advanced as more data are obtained and analyzed. Detailed chemical models can serve to improve our understanding and basis for the formulation of empirical parameterizations which reflect the underlying physical-chemical processes rather than merely expressing statistical correlations. Adherence to mechanistic considerations is recommended in formulating the parameterizations. More, and more reliable, measurements of such important variables as the atmospheric concentrations of OH, H_2O_2 , NH_3 , HC's, SO_4^{2-} and NO_3^- and of cloud dimensions and cloud chemical composition are needed direly.

H_2SO_4 and HNO_3 formations apparently peak during daytime and in summer. Gas-phase mechanisms are believed to contribute a larger share, on the average, to these secondary formations under warm, sunny conditions. Typically, on a summer day (24 hr) in the eastern United States, about 25 ± 10 percent of the airborne SO_2 in power plant plumes is likely to be converted to sulfates. Nighttime conversion is a small part (about 5 percent or less). S transformations may be somewhat higher than these in the southeastern United States. HNO_3 formation rate in power plant plumes is about three times as fast as the sulfate formation rate by gas-phase mechanisms. Aerosol NO_3^- formation rate is apparently very small, at least in the summer. Both sulfate and nitrate formation are faster in urban plumes.

- At this time, the major sources of uncertainty in determining atmospheric transport ranges of pollutants are probably associated with transport and deposition processes rather than with transformation processes.

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